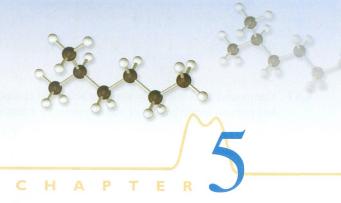
Functional Groups and Nomenclature I



HAPTER 2 showed that the number of organic compounds is virtually limitless. Functional groups were introduced as a useful method for organizing this vast number of compounds because chemical reactions occur at the functional group and compounds with the same functional group undergo similar reactions. Because functional groups are so important, we need to learn more about them. This chapter discusses approximately half of the functional groups in more detail. (A similar treatment of the remainder is provided in Chapter 12.) The physical properties (melting points, boiling points, and solubilities), natural occurrence, and uses of each of these functional groups are presented.

One of the major topics to be discussed in this chapter is organic nomenclature. Every compound needs a name that can be used in talking or writing about it. Once a compound is identified by a unique name, it is then possible to look it up in reference books (such as the *Handbook of Chemistry and Physics* or *Chemical Abstracts*) to find its reported physical and chemical properties. Therefore, a systematic method for naming simple organic compounds is presented. As you might expect, this method is organized on the basis of functional groups.

5.1 ALKANES

Organic compounds containing only carbon and hydrogen are called **hydrocarbons**. (In addition to alkanes, the class of hydrocarbons includes alkenes, alkynes, and aromatic compounds that have no additional functional group.) The bonds between the carbons of **alkanes**, the simplest type of hydrocarbons, are all single bonds; alkanes do not have

MASTERING ORGANIC CHEMISTRY

- Naming Alkanes Using Systematic Nomenclature
- Drawing the Structure of an Alkane from the Name
- Naming Complex Alkyl Groups
- Naming Cycloalkanes, Alkenes, Alkynes, Alkyl Halides, Alcohols, Ethers, and Amines
- Drawing Structures from the Names of These Compounds
- Predicting Approximate Physical Properties of Compounds with These Functional Groups

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any double or triple bonds. Alkanes fit the formula C_nH_{2n+2} , so they have a DU of zero. They have no functional group. **Cycloalkanes** are quite similar to alkanes with the exception that they contain rings of carbon atoms. Rings of five, six, and seven carbons are most common. Small rings (three and four carbons) are rarer. Larger rings (those with more than seven carbons) become increasingly less common as their size increases.

$$\begin{array}{cccc} CH_2 & H_2C & CH_2 \\ CH_3CH_2CH_2CH_3 & H_2C & CH_2 \\ & & & & \\ Pentane, & Cyclohexane, \\ an alkane & a cycloalkane \\ \end{array}$$

As you should recall from Chapter 2, the electronegativities of carbon and hydrogen are similar enough that carbon–carbon and carbon–hydrogen bonds have insignificant bond dipoles. Alkanes and cycloalkanes are nonpolar compounds. The only intermolecular interactions are London forces (instantaneous dipole-induced dipole) and are weak. For this reason, alkanes have low melting points and low boiling points. As shown in Table 5.1, methane boils at -162° C and therefore is a gas at room temperature. Boiling points and melting points increase with increasing molecular weight because London forces increase with increasing surface area. Pentane is the smallest alkane that is liquid at room temperature. Very large alkanes, such as eicosane ($C_{20}H_{42}$), are waxy solids. (Beeswax contains $C_{31}H_{64}$.) In general, cycloalkanes melt at significantly higher temperatures than their noncyclic counterparts because they are more symmetrical (compare hexane and cyclohexane in Table 5.1). Cycloalkanes also boil at somewhat higher temperatures.

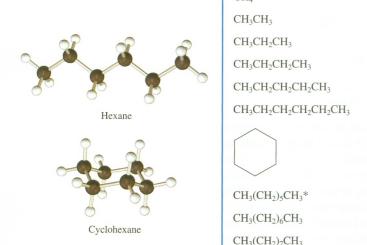
Because of their nonpolar nature, alkanes are insoluble in water. They are hydrophobic (water-hating) compounds. They are composed of atoms of lower mass (C and H) than water (O and H), so liquid alkanes are less dense than water. A mixture of water and a liquid alkane forms two layers, with the alkane as the upper layer. Many of the solvents that are used in the organic laboratory are compounds composed mainly of carbon and hydrogen, and so they tend to be less dense than water. Solvents whose molecules contain a significant fraction of more massive elements, such as chlorine, are more dense than water.

Alkanes are rather unreactive compounds and are sometimes called **paraffins** (from the Latin for "little affinity"). They have strong C—C and C—H bonds, which are hard to break. All their electron pairs are in relatively stable sigma bonding MOs. They have no polar sites or unshared electrons to attract Lewis acid or base reagents. They are extremely weak proton acids. Therefore, only a few of the reactions covered in this text involve alkanes.

Section 2.7 showed that it is often convenient to view a molecule as being composed of two parts: the functional group, where reactions occur, and the alkyl group, sometimes called the backbone of the compound. The alkyl group is just the "alkane" part of the molecule and, like alkanes, does not tend to enter into reactions. In most cases it does not matter what the exact structure of the alkyl group is, because the reactions occur at the functional group.

Alkanes occur in nature in deposits of natural gas and oil. Natural gas is primarily methane, containing progressively smaller amounts of ethane, propane, and butanes. Petroleum is a complex mixture of alkanes and other hydrocarbons. Petroleum is refined by distillation. The various distillation cuts, based on boiling point, are shown in Table 5.2.

Table 5.1 Physical Properties of Some Alkanes



Compound	Name	Melting Point (°C)	Boiling Point (°C)
CH ₄	Methane	-183	-162
CH ₃ CH ₃	Ethane	-183	-89
CH ₃ CH ₂ CH ₃	Propane	-187	-42
CH ₃ CH ₂ CH ₂ CH ₃	Butane	-138	-0.5
CH ₃ CH ₂ CH ₂ CH ₂ CH ₃	Pentane	-130	36
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	Hexane	-94	69
	Cyclohexane	6.5	80
CH ₃ (CH ₂) ₅ CH ₃ *	Heptane	-91	98
CH ₃ (CH ₂) ₆ CH ₃	Octane	-57	126
$CH_3(CH_2)_7CH_3$	Nonane	-51	151
CH ₃ (CH ₂) ₈ CH ₃	Decane	-30	174
CH ₃ (CH ₂) ₁₈ CH ₃	Eicosane	36	345

*The shorthand used to represent the longer chain alkanes: $CH_3(CH_2)_5CH_3$ means that there are five CH_2 's between the CH_3 's; the carbon chain has a total of seven carbons.

Table 5.2 Boiling Points for the Distillation Cuts of Petroleum

Distillation Cut	Boiling Point	Comment
Natural gas	Below 20°C	C_1 – C_4 alkanes; used primarily in industry and as a fuel for heating homes
Light petroleum and ligroin	20-120°C	C_5 – C_7 compounds; large amounts are heated to crack them to small alkenes, a major feedstock for the chemical industry
Gasoline	100–200°C	C ₇ -C ₁₀ compounds; contain a large fraction of straight-chain alkanes, which tend to detonate or "knock" when burned; heating over a catalyst breaks bonds, which re-form to produce branched alkanes, which burn more smoothly
Kerosene	200–300°C	C_{12} – C_{18} compounds; used as jet fuel and diesel fuel
Gas oil and lubricating oil	Above 300°C	Larger alkanes; used as heating and lubricating oils; large amounts are used to produce gasoline by heating over a catalyst in a process called <i>cracking</i>
Residue	Nonvolatile	Asphalt and bitumen

The most important use of alkanes is as fuels for combustion processes to produce heat and power:

$$C_n H_{2n+2} + (3n+1)/2 O_2 \longrightarrow n CO_2 + (n+1) H_2O + heat$$

Enormous amounts of natural gas and petroleum products are burned daily. Of course, in the combustion process, it is the heat produced that is more important, not the chemical products of the reaction, carbon dioxide and water. However, many scientists are concerned that the production in this reaction of enormous quantities of carbon dioxide, a greenhouse gas, might be initiating a global warming trend.

In the chemical laboratory the major use of alkanes is as solvents. Their property of being chemically unreactive makes them attractive solvents for many reactions because they will not interfere with the desired chemistry. However, their usefulness is limited because they will not dissolve highly polar or ionic compounds because of their completely nonpolar nature.

5.2 Common Nomenclature of Alkanes

The number of organic compounds is virtually limitless. Each needs a name that can be used in discussing the compound or writing about it. Furthermore, it is often necessary to look up the properties of a compound. (You should find out the physical properties of all the compounds that you use in the laboratory.) Very large tables of compounds and indexes use alphabetical listings of compound names.

In the early days of organic chemistry a newly discovered compound was often named according to the source from which it was isolated. The four-carbon carboxylic acid that was isolated from rancid butter was called butyric acid, after *butyrum*, the Latin word for butter. Even the early organic chemists realized the need to be systematic in naming compounds, so the four-carbon alkane that can be prepared from butyric acid was called butane. When an isomeric four-carbon alkane was discovered, it was called isobutane. Butane is a **straight-chain** or **unbranched** alkane. Such alkanes are termed **normal** and in the past were written with a prefix *n*-. Another name, then, that you may encounter in older sources for butane is *n*-butane. However, the *n*- is redundant today because the absence of any prefix implies an unbranched alkane, and it should not be used. Isobutane is a **branched** alkane. There are three isomeric alkanes with five carbons. The unbranched one is called pentane. The one with a single branch is called isopentane. The remaining isomer requires a different prefix. It is called neopentane.

These names are called **common** or **trivial** names. As the size of the alkane increases, the number of isomers increases dramatically. It would be very cumbersome to continue this process of providing different prefixes for each isomer of a larger alkane.

Furthermore, the task of learning all these prefixes would be daunting indeed. Decane has 75 isomers! Obviously, a systematic nomenclature is needed.

5.3 Systematic Nomenclature of Alkanes

A systematic method for naming alkanes (and other organic compounds) that is simple to use and minimizes memorization was developed by the International Union of Pure and Applied Chemistry and is called the IUPAC nomenclature. To make it easier for the chemists of that time to learn, it incorporated common nomenclature wherever possible.

Before we look at the steps for naming alkanes, let's see what an IUPAC name looks like. Basically, each alkane is considered a straight-chain carbon backbone on which

Focus On

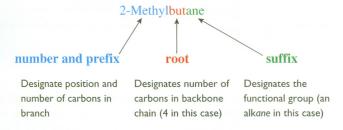
The Energy Content of Fuels

The amount of heat produced by burning (heat of combustion) varies considerably with the type of fuel that is burned. Values for some fuels of interest, in kilocalories (or kilojoules) per gram, are shown in the table that follows.

Some interesting observations can be made from these data. Hydrogen contains considerably more energy per gram than the other fuels. This is because the mass of a hydrogen atom is considerably less than that of a carbon or an oxygen atom, so 1 g of hydrogen contains many more molecules than 1 g of the other fuels. The energy contents of methane, butane, and cyclohexane, typical alkanes, are all similar. (There is a slight decrease in energy content as the percentage of hydrogen decreases from methane to butane to cyclohexane.) Part of the reason why benzene produces less energy than cyclohexane.

Compound	Heat Evolved kcal/g (kJ/g)	Compound	Heat Evolved kcal/g (kJ/g)
H_2	34.2 (143)	Coal	7.6 (32)
CH ₄ Methane	13.4 (56)	CH ₃ CH ₂ OH Ethanol	7.2 (30)
CH ₃ CH ₂ CH ₂ CH ₃ Butane	12.0 (50)	CH ₃ OH Methanol	5.5 (23)
	11.2 (47)	Wood	4.5 (19)
Cyclohexane		190310 .80	
Benzene	10.0 (42)	O OH OH OH OH OH HC—CH—CH—CH—CH—CH ₂	3.8 (16)

various branches or groups are attached. The IUPAC name for isopentane is 2-methylbutane. This name consists of a root that designates the number of carbons in the backbone, a number and a prefix that designate the position of the branch on the backbone and the number of carbons in the branching group, and a suffix that designates the functional group.



hexane is that benzene has a large resonance stabilization energy. Because benzene is more stable, it produces less heat when burned (more on this in Chapter 16).

One definition of **oxidation** often used in organic chemistry is an increase in the oxygen content of a compound. Combustion is, then, an oxidation process. As can be seen from the heats of combustion of the alkanes as compared to those of ethanol, methanol, and glucose, increasing the initial oxygen content of a compound—that is, increasing its oxidation state—results in a lower energy content. Methanol, for example, can be viewed as resulting from partial oxidation of methane. In methanol there are only three carbon—hydrogen bonds to "burn," compared to four in methane, so the energy content per mole is less for methanol. (The energy content is even less on a per gram basis.)

Gasoline is composed primarily of alkanes, so its energy content is in the 11 to 12 kcal/g (46–50 kJ/g) region. This relatively high energy content makes gasoline an attractive fuel for automobiles. Of course, hydrogen is even better in terms of energy content and burns with less pollution. However, it is much more difficult to handle. Methanol has been proposed as an alternative to gasoline. One drawback is that its energy density is much less than that of gasoline, which means that the miles per gallon would drop substantially if methanol were used. The use of oxygenated gasoline, usually containing 10% or more of ethanol or *methyl tert-butyl ether* (MTBE), is mandated in many cities during the winter months because it purportedly reduces pollution due to carbon monoxide. If you live in such an area, you may notice a small decrease in your gas mileage during the winter.

Glucose is a common sugar. Its structure is similar to that of other sugars. Carbohydrates, such as starch, are composed of a large number of glucose units. Therefore, the energy content of glucose is representative of the energy content of a major part of our food. The energy content of glucose is low because of its highly oxygenated structure. It supplies 3.8 kcal/g (16 kJ/g) of energy. Note that the "Calorie" (written with an uppercase C) that is used in nutrition is actually a kilocalorie, so sugars and carbohydrates have about 4 Calories per gram. You may have heard that alcoholic beverages are quite fattening. Ethanol, the alcohol contained in beverages, has nearly twice the energy density of sugar because it contains significantly less oxygen. It supplies 7 Calories per gram.

Table 5.3 Names for the Roots That Designate the Number of Carbons in the Backbone Chain

Number of Carbons	Root
I	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-
7	hept-
8	oct-
9	non-
10	dec-
Ш	undec-
12	dodec-
13	tridec-
14	tetradec-
15	pentadec-
20	eicos-
21	heneicos-
22	docos-
23	tricos-
30	triacont-

The roots for backbones containing one through four carbons come from the common names for these alkanes. You probably recognize most of these already. For backbones of five or more carbons, systematic roots (derived from Greek) are employed.

Now let's discuss how to name an alkane by the IUPAC method.

STEP I

Find the longest continuous carbon chain in the compound. The number of carbons in this backbone determines the root (see Table 5.3). If there are two (or more) chains of equal length, choose the one with the greater number of branches. (This results in simpler branching groups that are easier to name.)

It is important to realize that the name of a compound must not depend on how that compound is drawn. When a drawing for a compound is encountered, the longest continuous chain will not necessarily be shown in a straight, horizontal line. Each structure must be carefully examined to identify the longest chain, no matter how it bends and curls around. Some examples, with the longest chain in red, follow:

There are two different six-carbon chains for this compound. Choose the chain as shown in the left structure because it has two branches rather than in the right one, which has only one branch. The root is hex-.

STEP 2

Attach the suffix. For alkanes, it is -ane.

Steps 1 and 2 are all that are needed to name unbranched alkanes. For example, the straight-chain alkane with seven carbons is heptane.

Heptane

To name branched alkanes, additional steps to name the branching group and locate it on the root chain are needed.

STEP 3

Number the carbons in the root chain. Start from the end that gives the lower number to the carbon where the first branch occurs. If both ends have the first branch at equal distances, choose the end that gives the lower number to the carbon where the next branch occurs.

Examples include the following:

For this structure, the correct numbering starts with the right carbon. Then the first branching group is attached to C-2. Incorrect numbering, starting with the left carbon, would result in the first branch being attached to C-4.

For this structure, the correct numbering starts with the left carbon. The first branch is attached to C-2 and the second branch to C-4. If numbering were to begin with the right carbon, the first branch would be attached to C-2, but the second would be attached to C-5.

$$\begin{array}{c|cccc} CH_3 & CH_3 \\ | & | & \\ CH_3CHCH_2CH_2CCH_3 \\ 6 & 5 & 4 & 3 & 2 \mid 1 \\ CH_3 \end{array}$$

For this structure, the correct numbering starts with the right carbon. The first branch is at C-2 regardless of whether the starting point is the right carbon or the left carbon. However, the second branch is also at C-2 when the starting point is the right carbon. It occurs at C-5 when the starting point is the left carbon.

In other words, proceed inward, one carbon at a time, from each end of the root chain. At the first point of difference, where a group is attached to one carbon under consideration but not the other, choose the end nearer that carbon with the attached group to begin numbering.

STEP 4

Name the groups attached to the root. For straight-chain groups, use the same roots as before to designate the number of carbons and add the suffix -yl.

$$\mathrm{CH_3-}$$
 $\mathrm{CH_3CH_2-}$ $\mathrm{CH_3CH_2CH_2CH_2-}$ Methyl Ethyl Pentyl

A group can be pictured as arising from an alkane by the removal of one hydrogen. It is not a complete compound by itself but requires something to be attached to the remaining valence.

STEP 5

Assemble the name as a single word in the following order: number, group, root, and suffix. Note that a hyphen is used to separate numbers from the name.

$$\begin{array}{c} \text{CH}_3\\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_3\\ 6\quad 5\quad 4\quad 3\quad 2\quad 1 \end{array} \qquad \text{3-Methylhexane}$$

If several different groups are present, list them alphabetically. If there are several identical groups, use the prefixes di-, tri-, tetra-, and so on to indicate how many are present. A number is required to indicate the position of each group. For example, 2,2,3-trimethyl indicates the presence of three methyl groups, two attached to C-2 of the backbone and one attached to C-3. Do not use the prefixes that denote the number of groups for alphabetizing purposes. For example, triethyl is listed under e and so comes before methyl in a name.

Let's use these steps to name the following compound:

$$\begin{array}{c|ccccc} CH_3 & CH_2CH_3 & CH_3 \\ & & & & \\ CH_3CHCH_2CHCH_2CH_2CHCH_3 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \end{array}$$

4-Ethyl-2,7-dimethyloctane

Previously, it was determined that the longest chain has eight carbons (so the compound is a substituted octane) and that numbering should begin with the leftmost carbon. Three goups are attached to the root chain: two methyl groups and an ethyl group. Therefore the systematic or IUPAC name is 4-ethyl-2,7-dimethyloctane. Note the use of hyphens to separate numbers from letters and the use of commas to separate a series of numbers. Also note that dimethyl is alphabetized under m (not d) and so is listed after ethyl in the name.

PROBLEM 5.1

Provide IUPAC names for these alkanes:

PRACTICE PROBLEM 5.1

Draw the structure of 2,2,5-trimethylheptane.

Strategy

Drawing the structure of a compound when the name is provided is usually a straightforward process. First draw a chain with the number of carbons indicated by the root. Number the chain starting at either end and add the appropriate groups at the appropriate positions.

Solution

The root is hept-, so draw a chain of seven carbons. Number the chain and add three methyl groups: two on C-2 and one on C-5.

$$\begin{array}{cccc} CH_3 & CH_3 \\ | & | \\ CH_3CCH_2CH_2CHCH_2CH_3 \\ 1 & 2 \mid 3 & 4 & 5 & 6 & 7 \\ CH_3 & & & \end{array}$$

PROBLEM 5.2

Draw the structures of these compounds:

- a) 4-Methyloctane
- b) 2,4-Dimethyl-5-propyldecane

PRACTICE PROBLEM 5.2

What is wrong with the name 2-ethylpentane? Provide the correct name for this compound.

Solution

First, let's draw the structure suggested by the name:

Examination of this structure shows that the longest chain has six carbons rather than five. Therefore, the correct name is 3-methylhexane.

PROBLEM 5.3

What is wrong with these names? Provide the correct name for each.

- a) 5,5-Dimethyl-3-ethylhexane
- b) 2-Dimethylpentane

Often groups attached to the root chain are branched rather than the straight-chain ones encountered so far. Such complex groups are named in a fashion similar to that used to name compounds, but with a -yl ending to indicate that they are not complete

$$\begin{array}{c|ccccc} CH_3 & CH_3 \\ & & 5 & \\ CH_3CHCH_2CH_2CHCH_2CHCH_3 \\ 1 & 2 & 3 & 4 & \\ & & & CH_2CH_2CH_2CH_3 \\ & & & & 6 & 7 & 8 & 9 \end{array}$$

The longest chain in this compound (in red) has nine carbons. Numbering begins at the left carbon because the first group is then encountered at position 2. The group (in blue) bonded to position 5 has a branch. The compound is named as a substituted nonane, but how is the complex group at position 5 named?

Here is the group. It is named in a manner similar to that used to name alkanes. The longest chain that begins with the carbon attached to the main chain is chosen. As before, the root is determined by the number of carbons in this longest chain (three in this case). The suffix -yl is used to indicate that this is a group rather than a complete compound. So this group is named as a substituted propyl group. Numbering the root chain of a complex group is easy. The carbon attached to the main chain is number 1. The name of the complex group is 2-methylpropyl-.

The name for the complex group is placed in parentheses to avoid confusion when the entire compound is named. The number designating the position of the complex group on the main chain is placed outside the parentheses. Therefore, the name of the compound is 2-methyl-5-(2-methylpropyl)nonane.

Figure 5.1

Naming a compound with a complex group.

compounds and need to be attached to something to complete their bonding. Naming complex groups is described in Figure 5.1.

PRACTICE PROBLEM 5.3

What is the name of this complex group?

Strategy

Choose the longest chain that begins at the carbon attached to the main chain. Number this chain with the carbon attached to the main chain receiving number 1. Add the groups attached to this chain with the numbers indicating their positions. When the full name of the compound is written, do not forget to place the entire complex group name in parentheses preceded by a number indicating the position of the group on the main chain.

Solution

In this case the longest chain has five carbons. When the numbering starts at the carbon attached to the main chain, the methyl group is on C-4, so the name of the group is (4-methylpentyl).

PROBLEM 5.4

Provide names for these complex groups:

PROBLEM 5.5

Name these compounds:

PRACTICE PROBLEM 5.4

Draw a structure for 4-(1,1-dimethylethyl)decane.

Solution

The compound is a decane, so there are 10 carbons in the main chain. On C-4 there is an ethyl group that has two methyl groups attached to the carbon that is attached to the decane chain:

PROBLEM 5.6

Draw structures for these compounds.

- a) 4-(1-Methylethyl)heptane
- b) 3-Ethyl-7-methyl-5-(1-methylpropyl)undecane

Some additional terminology permeates organic chemistry and must be part of every organic chemist's vocabulary. The chemical reactivity of a carbon or of a functional group attached to that carbon often varies according to the number of other carbons bonded to it. In discussions of chemical reactivity, therefore, it is often useful to distinguish carbons according to how many other carbons are bonded to them. A **primary carbon** is bonded to one other carbon, a **secondary carbon** is bonded to

two carbons, a **tertiary carbon** is bonded to three carbons, and a **quaternary carbon** is bonded to four carbons. The following compound contains each of these types of carbons:

PROBLEM 5.7

Designate each carbon of these compounds as primary, secondary, tertiary, or quaternary:

c) 2,3-Dimethylpentane

Finally, in addition to the systematic method for naming groups that we have just seen, we will still encounter some common group names. IUPAC nomenclature allows the use of these common group names as part of the systematic name. (IUPAC nomenclature does allow different names for the same compound; however, no two compounds may have the same name.) Table 5.4 shows a number of groups, along with their systematic names, their common names, and abbreviations that are sometimes used to represent the groups when writing structures. (The abbreviations are not used in nomenclature.) There are four butyl groups in the table. To help remember them, note that the *sec*-butyl group is attached via a secondary carbon and the *tert*-butyl group is attached via a tertiary carbon. The italicized prefixes *sec*- and *tert*- are not used in alphabetizing; *sec*-butyl is alphabetized under *b*. However, isobutyl is alphabetized under *i*.

PROBLEM 5.8

Name this compound using the common name for the group:

PROBLEM 5.9

Draw the structure of 4-tert-butyl-2,3-dimethyloctane.

Table 5.4 Systematic Names, Common Names, and Abbreviations for Some Groups

Group	Systematic Name	Common Name	Abbreviation
СН3—	Methyl		Me
CH ₃ CH ₂ —	Ethyl		Et
CH ₃ CH ₂ CH ₂ — CH ₃	Propyl		Pr
CH ₃ CH—	I-Methylethyl	Isopropyl	i-Pr
CH ₃ CH ₂ CH ₂ CH ₂ —	Butyl		Bu
CH_3	reservo		
CH ₃ CHCH ₂ —	2-Methylpropyl	Isobutyl	i-Bu
rbanoan CH ₃			NAME OF THE PROPERTY OF THE PR
CH ₃ CH ₂ CH—	I-Methylpropyl	sec-Butyl	sec-Bu (or s-Bu)
CH ₃	The control of the co		
CH ₃ C—	1,1-Dimethylethyl	tert-Butyl	tert-Bu (or t-Bu)
CH_3			
—CH ₂ —	The state of the s	Methylene	
	Phenyl		Ph

The common names may be used in IUPAC nomenclature.

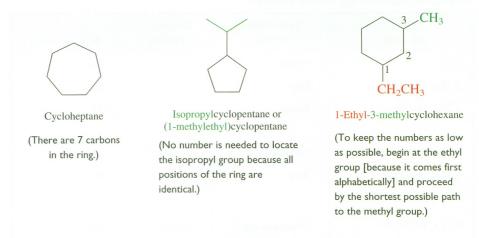
5.4 Systematic Nomenclature of Cycloalkanes

The procedure used to name a cycloalkane by the IUPAC method is very similar to that used for alkanes. Here, the root designates the number of carbons in the ring and the prefix cyclo- is attached to indicate that the compound contains a ring. The rules for numbering the ring carbons are as follows:

No number is needed if only one group is attached to the ring.

For rings with multiple substituents, begin numbering at one substituent and proceed in the direction that gives the lowest numbers to the remaining substituents.

Some examples follow:



In cases in which the alkyl chain has more carbons than the ring, the compound is named as an alkane with the ring as a substituent group with a -yl suffix.

1-Cyclobutyl-2-methylpentane

(There are five carbons in the longest alkyl chain, whereas the ring has only four carbons. Therefore, the ring is named as a substituent group on the alkane chain.)

PROBLEM 5.10

Name the following compounds:

PROBLEM 5.11

Draw structures for these compounds:

- a) 1,1-Dimethylcyclohexane
- b) Ethylcyclopropane

5.5 ALKENES

Alkenes have one or more carbon—carbon double bonds. In the discussion in Chapter 2 about calculating the degree of unsaturation of a compound, it was shown that each double bond present in an alkene results in a decrease of two hydrogens in the formula when compared to an alkane with the same number of carbons. The term unsaturated is used to describe alkenes and actually has a chemical derivation. It is possible to cause compounds containing double or triple bonds to react with hydrogen gas to form alkanes. When the compound will no longer react with hydrogen, it is said to be saturated. A compound that will react with hydrogen, such as an alkene or an alkyne, is, then, unsaturated. You have probably heard these terms used a lot in association with cooking oils or margarines. A polyunsaturated oil is composed of compounds that contain several carbon—carbon double bonds. A saturated fat, by contrast, is composed of similar compounds that have no double bonds.

Alkenes are named similarly to alkanes, with the following modifications:

- 1. The longest continuous chain that includes both carbons of the double bond provides the root.
- **2.** The suffix used for an alkene is -ene. Names for compounds with more than one double bond use the suffixes -diene, -triene, and so on.
- 3. The root is numbered from the end that gives the lower number to the first carbon of the double bond. The number of this first carbon is used in the name to designate the position of the double bond. This number may be placed before the root or between the root and the suffix.

Some examples include the following:

4-Methyl-2-pentene or 4-methylpent-2-ene

(The double bond, not the methyl group, determines the numbering.)

3-Ethyl-4-methylcyclohexene

(Numbering begins with the carbons of the double bond having numbers I and 2 and proceeds in the direction that will give the lowest numbers to the remaining substituents. Because the double bond of a cycloalkene is always located at position I, the I is usually not used. However, some sources do specifically designate the position of the double bond when other groups are present on the ring. Thus, this compound is also properly named 3-ethyl-4-methylcyclohex-I-ene. We will omit the I in such situations in this book.)

4-Isopropyl-1,3-heptadiene or 4-isopropylhepta-1,3-diene

(Note the *a* in heptadiene. This is added to the root whenever the first letter of the suffix is a consonant to make the name easier to pronounce.)

2-Ethyl-1-pentene or 2-ethylpent-1-ene

(Both carbons of the double bond must be part of the root chain.)

PRACTICE PROBLEM 5.5

Name this alkene:

$$\begin{array}{c} CH_3 \\ | \\ CH_2 = CHCHCH_2CHCH_3 \\ | \\ CH_2CH_2CH_3 \end{array}$$

Solution

Choose the longest chain that contains both of the carbons of the double bond (first priority) and has the most branches (second priority):

Number it beginning at the left end so that the carbons of the double bond have lower numbers. It has a propyl group on C-3 and a methyl group on C-5, so the name is 5-methyl-3-propyl-1-hexene.

PROBLEM 5.12

Name these compounds:

PROBLEM 5.13

Draw structures for these compounds:

- a) 3-Ethyl-3-hexene
- b) Cyclobutene
- c) 3-Propyl-cyclohexa-1,4-diene

Table 5.5	Common Names for Some	
Compound	ds and Groups Containing	
Double Bo	nds	

Compound or Group	Common Name
$CH_2 = CH_2$	Ethylene
$CH_2 = CHCH_3$	Propylene
$CH_2 = CHCH_2CH_3$	Butylene
CH_3	
$CH_2 = CCH_3$	Isobutylene
$CH_2 = C = CH_2$	Allene
CH ₂ =CH-	Vinyl group
CH ₂ =CHCH ₂ -	Allyl group

A few of the common names that are often encountered for alkenes and groups containing double bonds are listed in Table 5.5.

The polarity of an alkene is not much different from the polarity of an alkane. Therefore, the physical properties of an alkene are similar to those of the corresponding alkane. For example, 1-pentene melts at -138° C and boils at 30° C, values that are comparable to those of pentane, which melts at -130° C and boils at 36° C.

However, the chemical properties of an alkene are dramatically affected by the presence of the double bond. Recall that a carbon—carbon pi bond is considerably weaker than a carbon—carbon or carbon—hydrogen sigma bond. It is possible to selectively cause a reaction to occur at a pi bond under conditions that do not affect the sigma bonds. The pi bond is the weak spot of an alkene, and it is there that most chemical reactions occur. This is why unsaturated fats spoil more readily than saturated fats. Their pi bonds provide a place for reaction with oxygen to occur, which leads to spoilage.

Alkenes occur in nature, especially among a group of natural products called terpenes that occur in plants. Examples are limonene, which is found in citrus fruits and caraway seeds, and β -carotene, a highly conjugated molecule that is the orange pigment found in carrots and is an important precursor of vitamin A. Interestingly, even the simplest alkene, ethene, has an important role in nature. Ethene has been found to be a plant hormone that causes ripening in fruits.

The two simplest alkenes, ethylene (ethene) and propylene (propene), are the organic compounds that are produced in the largest amounts by the U.S. chemical in-

dustry. More than 48 billion pounds of ethylene and more than 28 billion pounds of propylene are produced annually by cracking of hydrocarbons ranging from ethane to heavy gas oil. These alkenes then serve as feedstocks for the production of plastics, such as polyethylene and polypropylene, as well as starting materials for the preparation of numerous other commercial chemicals, such as ethylene glycol (antifreeze).

5.6 ALKYNES

Alkynes are compounds that have a carbon—carbon triple bond. As was discussed in Chapter 3, a triple bond is composed of one sigma bond and two pi bonds. Each triple bond in an alkyne causes it to have four fewer hydrogens than the corresponding alkane. Alkynes are unsaturated compounds.

Alkynes are named in a manner nearly identical to the naming of alkenes except that the suffix is -yne. The same rules for numbering apply. Compounds with several triple bonds use the suffixes -diyne, -triyne, and so on. For compounds that contain both a double bond and a triple bond, both suffixes are used, as in -enyne. Some examples follow:

HC≡**CH**

Ethyne or acetylene (Acetylene is the common name. Alkynes as a class are sometimes called acetylenes.)

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{C} = \text{CCH}_2\text{CH}_2\text{CHCH}_3\\ 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \\ \\ \text{7-Methyl-3-octyne} \\ \text{or} \\ \text{7-Methyloct-3-yne} \end{array}$$

 CH_3

(Number so that the first C of the triple bond gets the lowest number.)

$$CH_{2}-CH_{2}CH_{2}-CH_{2}$$
 $CH_{2}-CH_{2}-CH_{2}$
 $CH_{2}-CH_{2}$
 $CH_{2}-CH_{2}$

1-Cyclodecen-4-yne or cyclodec-1-en-4-yne

(When there is an equal choice in numbering, double bonds are given lower numbers than triple bonds.)

$$HC = C - CH = CH - CH = CHCH_3$$
1 2 3 4 5 6 7

3,5-Heptadien-1-yne or hepta-3,5-dien-1-yne

(Numbers as low as possible are given to the double and triple bonds even though this results in the triple bond having the lower number. Note the locations in the name of 3 and 5, which refer to diene, and I, which refers to -yne.)

PROBLEM 5.14

Name these compounds:

a)
$$HC \equiv CCHCH_2CH_2CH_3$$
 b) $CH_3C \equiv C-C=CH_2$

PROBLEM 5.15

Draw structures for these compounds:

a) 1-Pentyne b) 2,3,4-Trimethyl-5-undecyne

As might be expected, the physical properties of alkynes are very similar to those of alkenes and alkanes with the same number of carbons. For example, the boiling points of hexane, 1-hexene, and 1-hexyne are 69°C, 63°C, and 71°C, respectively.

Because of their pi bonds, the chemical properties of alkynes are very similar to those of alkenes. They undergo many of the same reactions as alkenes and often react at both pi bonds.

Alkynes are less common in nature than are alkenes. Alkynes are also less important in industry. The largest use of acetylene is as a fuel for the oxyacetylene welding torch, which burns at a very high temperature.

5.7 ALKYL HALIDES

The halogens have the same valence as hydrogen. Organic compounds with one or more halogens in place of hydrogens are called **alkyl halides.** These compounds are named as alkanes with the halogen as a substituent. The group names for the halogens are fluoro-, chloro-, bromo-, and iodo-. We may also encounter common names for simple alkyl halides. These use the name of the alkyl group followed by the name of the halogen.

PROBLEM 5.16

Name these compounds:

Click Coached Tutorial Problems to practice Naming Alkanes, Alkenes, and Cycloalkanes or to practice Drawing Structures of these compounds.

PROBLEM 5.17

Draw the structure of 3-bromo-4-butylcyclohexene.

The carbon-halogen bond is slightly polar. Overall, however, an alkyl halide is not much more polar than an alkane, so the physical properties of an alkyl halide are not very different from those of an alkane of similar molecular weight. For example, the boiling point of 1-chlorobutane (MW = 92.5 g/mol) is 78°C, whereas that of hexane (MW = 86 g/mol) is 69°C. In general, alkyl halides are insoluble in water. Because of the presence of the more massive halogen atom, the alkyl halide may be more dense than water. For example, when dichloromethane, a common laboratory solvent, and water are mixed, two layers are formed, with dichloromethane as the lower layer.

Halogenated organic compounds are of great industrial importance. Those containing a number of halogens (polyhalogenated) are often chemically inert and thermally stable compounds that have found uses as refrigerants, industrial solvents, degreasers, aerosol propellants, and so on. Some examples include the following:

1 1	
CF ₂ Cl ₂	Chlorofluorocarbon 12, a freon, was used in refrigeration systems and air conditioners and as an aerosol propellant because of its high stability and low toxicity. Its stability results in environmental problems. It does not decompose until it reaches the upper atmosphere, where ultraviolet light causes the carbon–chlorine bonds to break. The resulting chlorine atoms catalyze the destruction of ozone, resulting in the infamous ozone hole. The use of this and other stable freons has recently been phased out.
CF₃Br	This compound is used in Halon fire extinguishers. Many polychloro and polybromo organics are used as flame retardants in various applications.

CCI ₃ CH ₃	1,1,1-Trichloroethane is the most common solvent used in the dry cleaning of
	clothes. Carbon tetrachloride (CCl ₄) was used in the past, but it has been found
	to come lives described and in equal paraming

to cause liver damage and is carcinogenic.

CF₃CHBrCl Halothane is a popular anesthetic. Chloroform, CHCl₃, was one of the first anesthetics, but, like carbon tetrachloride, it is toxic and causes liver damage.

5.8 Alcohols

Alcohols are compounds that contain a hydroxy group (-OH). Common names for simple alcohols use the name of the alkyl group followed by alcohol, such as ethyl alcohol or isopropyl alcohol. In the IUPAC system, alcohols are given the name of the hydrocarbon from which they are derived, with the suffix -ol replacing the final e of the name. The longest chain that contains the carbon bonded to the hydroxy group is chosen as the root and numbered so that this carbon has the lowest possible number.

2-Propanol or isopropyl alcohol

5-Methyl-3-propyl-2-hexanol

(The parent chain must contain the carbon bonded to the OH. The chain is numbered so that this carbon has the lower number.)

3,4-Dichloro-3-buten-2-ol

2-Cyclopentenol

(Note the position of the second 3, which refers to the carbon–carbon double bond, and the 2, which refers to the hydroxy group. Numbering is done to give the lower number to the OH, not the double bond. We say that the OH group has a higher priority than the double bond. The alternative style name, 3,4-dichlorobut-3-en-2-ol, makes the location of the double bond and the OH less likely to be confused.)

2-Methyl-1,4-cyclohexanediol or 2-methylcyclohexan-1,4-diol

(The suffix -diol is used to show the presence of two hydroxy groups; -triol is used for three, and so on.)

PROBLEM 5.18

Name these compounds:

c)
$$OH$$
 OH $CH_2CH_2CH_2$ OH CH_3

PROBLEM 5.19

Draw structures for these compounds:

- a) 2-Methylcyclohexanol
- b) 4-Methyl-4-penten-2-ol

Focus On Biological Chemistry

Chlorinated Organic Compounds

The use of chlorinated organic compounds in agriculture and industry has caused a number of environmental problems. A good illustration is provided by the case of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, better known as dichlorodiphenyl-trichloroethane, or DDT.

$$\begin{array}{c} Cl \\ Cl - C - Cl \\ H \end{array}$$

DDT was the first synthetic organic pesticide. Although it has received considerable negative publicity, it was probably the most useful insecticide ever developed. The story begins in 1939, when Dr. Paul Müller, a Swiss entomologist, discovered that DDT was extremely effective in controlling flies and mosquitoes. During World War II, DDT was used with great success in Italy against body lice that carry typhus and in the Pacific against mosquitoes that carry malaria. In 1948, Müller received the Nobel Prize in medicine for this discovery.

After the war the agricultural community in the United States used DDT enthusiastically. It had virtually ideal properties as an insecticide; it was effective against a wide variety of insects, it was not very toxic to mammals, it was persistent, and—very important—it was cheap, costing less than 22 cents per pound! In 1961, 160 million pounds of DDT were used in the United States.

However, two of the very properties of DDT that made it valuable as a pesticide led to it also becoming an environmental hazard. DDT is very stable—its biodegradation is very slow. Therefore, it accumulates in the environment. In addition, as examination of its structure suggests, DDT is very hydrophobic. It is very insoluble in water and quite soluble in nonpolar compounds. When an organism ingests DDT, the water insolubility of DDT greatly slows its excretion. Therefore, it accumulates in the organism, specifically in nonpolar regions such as fats or lipids. Thus, while the concentration of DDT in larvae in a lake, for example, may be low, the concentration in trout that feed on these larvae will be much higher because the trout will accumulate all the DDT in all the larvae that they consume. And the concentration in an eagle

that feeds on the trout will be higher still. This increase in concentration as one proceeds up the food chain is called biomagnification.

Rachel Carson called attention to the abuse and overuse of pesticides in her 1963 book *Silent Spring*. Decreases in the populations of some wildlife species, especially birds, were attributed to the relatively large concentrations of DDT that were found in them. In 1973 the Environmental Protection Agency banned the use of DDT in the United States. The appropriateness of this action has been hotly debated.

Supporters of the use of pesticides claim that there is not one reported instance of an adverse effect in a human caused by DDT and that it is one of the least toxic and safest of all pesticides to humans and animals. Because of its low cost and effectiveness, DDT is still widely used in countries where malaria is endemic. Some of these poorer countries regard DDT as a very important life-saver.

Regardless of one's position in this debate, it is apparent that the use of compounds that show persistence in the environment must be carefully examined and monitored. Any compound that is persistent and hydrophobic (lipophilic or fat soluble) will be subject to the process of biomagnification and may present special problems. In addition to DDT and other chlorinated pesticides, another example is provided by the polychlorinated biphenyls (PCBs). These compounds have two benzene rings bonded together, with varying numbers of chlorines substituted on the rings. One example is provided by the following structure:

(PCB)

PCBs are so chemically inert that they were extensively used as heat transfer fluids in large electrical transformers, along with other uses. Of course, when they escaped into the environment, they exhibited the two troublesome qualities of persistence and biomagnification. Because PCBs are now suspected carcinogens, they are no longer manufactured in the United States. However, they are now widely distributed in the environment. Furthermore, there is the problem of disposing of the large number of electrical devices that contain these compounds.

The chemical reactions of alcohols differ somewhat depending on how many carbons are attached to the carbon bearing the hydroxy group. Therefore, it is sometimes useful to classify alcohols as primary, secondary, or tertiary. A **primary alcohol** has the hydroxy group on a primary carbon, a **secondary alcohol** has the hydroxy group on a secondary carbon, and a **tertiary alcohol** has the hydroxy group on a tertiary carbon.

The physical properties of alcohols are dramatically affected by the presence of the hydroxy group. The polarity of the hydroxy group causes an alcohol to melt at a somewhat higher temperature than an alkane of similar molecular weight; compare the melting points of pentane and 1-butanol in the following table. The effect of the hydroxy group on the boiling point is substantially larger because of the ability of the hydroxy group to form hydrogen bonds, which must be broken in the vaporization process.

CH ₃ CH ₂ CH ₂ CH ₃	CH ₃ CH ₂ CH ₂ CH ₂ OH
Pentane	I-Butanol
72 g/mol	74 g/mol
mp - 130°C	mp −90°C
bp 36°C	bp II7°C

The hydroxy group is **hydrophilic** (water loving) because of its polarity and ability to form hydrogen bonds, so alcohols are much more soluble in water than alkanes. The smaller alcohols, containing up to three carbons, are miscible with water—that is, they mix with water in all proportions. As expected, as the alkyl group (the hydrophobic part) of the alcohol becomes larger, water solubility decreases. Thus, 1-pentanol dissolves in water to the extent of 2.7 g/100 mL and 1-heptanol to the extent of 0.1 g/100 mL, whereas 1-decanol is essentially insoluble in water.

Alcohols occur widely in nature. Methanol is also known as wood alcohol because it can be obtained by distilling wood in the absence of air. It is very poisonous and can cause blindness or death if ingested. Ethanol is consumed in alcoholic beverages. Other simple alcohols, such as 2-phenylethanol from roses and menthol from peppermint, are constituents of natural flavors and fragrances. Alcohols are important intermediates in chemical synthesis. They are also commonly used as solvents for various chemical processes. Ethylene glycol is used in antifreeze and in the preparation of polymers such as Dacron.

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{2}\text{CH}_{2}\text{OH} \\ \end{array} \begin{array}{c} \text{OH} \\ \text{OH} \\ \text{CH}_{3}\text{CHCH}_{3} \\ \end{array} \begin{array}{c} \text{OH} \\ \text{OH} \\ \text{CH}_{2}\text{-CH}_{2} \\ \end{array}$$
 2-Phenylethanol
$$\begin{array}{c} \text{Menthol} \\ \text{Menthol} \\ \end{array} \begin{array}{c} \text{Ethylene glycol} \\ \text{1,2-Ethanediol} \\ \end{array}$$

5.9 ETHERS

Ethers are compounds with two hydrocarbon groups bonded to an oxygen. Common names are often used for simple ethers. In these, each alkyl group is named, followed by the word *ether*. Thus, CH₃OCH₂CH₂CH₃ is methyl propyl ether. In systematic nomenclature the smaller alkyl group and the oxygen are designated as an **alkoxy** substituent on the larger group, which is named as an alkane. Complex ethers must be named by using the IUPAC system. However, IUPAC names for simple ethers are seldom used; diethyl ether (or ethyl ether) is rarely called ethoxyethane, although this name is certainly proper.

PROBLEM 5.20

Common

IUPAC

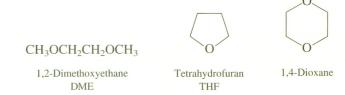
Name these compounds:

An ether is somewhat polar because of its carbon—oxygen bonds. However, its melting and boiling points are closer to those of a hydrocarbon of similar molecular weight than to those of an isomeric alcohol because of the inability of the ether to form hydrogen bonds. For example, the boiling point of diethyl ether (35°C) is close to that of pentane (36°C) and considerably lower than that of its isomer 1-butanol (117°C). However, the oxygen of an ether can participate as the Lewis base partner of a hydrogen bond. This results in the solubility of an ether in water being comparable to that of a similar alcohol. For example, the solubility of diethyl ether in water is 8.4 g/100 mL, whereas that of 1-butanol is 7.4 g/100 mL. As was the case with alcohols, the solubility of an ether in water decreases as the sizes of the alkyl groups increase.

You are probably aware that diethyl ether is the "ether" that has been used as an anesthetic. A major drawback is that ether is very flammable and volatile; mixtures of ether and air can be explosive. For this reason, ether has been replaced as an anesthetic by less hazardous compounds such as methoxyflurane:

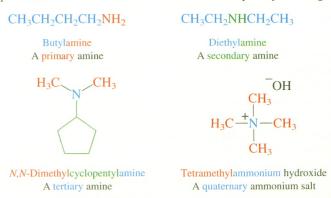
Methoxyflurane

A major use of ethers in the organic laboratory is as solvents for reactions. Ethers are nonpolar enough to dissolve many organic compounds, and the electrons on the oxygen can interact with alkali metal cations to help solubilize salts. In addition, ethers are nonacidic and are not very reactive. For these reasons they are especially useful in reactions involving strongly basic reagents. In addition to diethyl ether, other ethers that are commonly used as solvents are 1,2-dimethoxyethane (DME) and the cyclic ethers tetrahydrofuran (THF) and 1,4-dioxane:



5.10 Amines

Amines can be considered as derivatives of ammonia in which one or more hydrogens have been replaced by alkyl or aryl groups. **Primary amines** have one alkyl or aryl group bonded to the nitrogen. **Secondary amines** have two groups on the nitrogen, **tertiary amines** have three, and **quaternary ammonium salts** have four. Note that the terms *primary, secondary,* and *tertiary* have different meanings here than they have with other functional groups. In the case of amines they refer to the number of carbon groups bonded to the *nitrogen*. In the case of alcohols and alkyl halides, however, they refer to the number of carbon groups bonded to the *carbon* that is bonded to the hydroxy or halogen substituent.



Common names are usually employed for simple amines. In these names, the suffix -amine is appended to the name of the alkyl group. The prefixes di-, tri- and tetra- are used when several identical groups are attached to the nitrogen. For secondary and tertiary amines with different groups attached to the nitrogen, the largest group is used with the -amine suffix. An N-, rather than a number, is used to indicate other groups that

are also attached to the nitrogen. Ionic compounds that are formed by the reaction of amines with acids are named as ammonium salts. Common names for some amines are shown in the preceding examples and in those that follow:

There are many trivial names for amines, especially those involving aromatic rings or where the nitrogen is part of a ring. Several important examples are the following:

For more complex amines, systematic nomenclature is employed. Such names are constructed in a manner very similar to that employed to name alcohols. The largest chain attached to the nitrogen is chosen as the root, numbered so that the carbon attached to the nitrogen has the lower number, and the suffix -amine is attached. Other groups that are attached to the nitrogen are given the prefix N-.

attached to the nitrogen, it is given the prefix N-, rather than a number.)

In addition to carbon—carbon double and triple bonds, only one other functional group can be designated as a suffix in the name. For example, if a compound has both an alcohol and an amine functional group, only one of them can be designated with the suffix. The other must be named as a group, using a prefix. The alcohol functional group has higher priority than the amine functional group, so the nitrogen group is named as an amino- group (or an alkylamino- group) on the main chain of the alcohol. (The priorities and group names for other groups are listed in Table 12.3 on p. 492.) An example is provided by the following compound:

Click Coached Tutorial Problems to practice Drawing Structures of Alkyl Halides, Alcohols, Ethers, and Amines.

3-Ethylamino-2-methylcyclohexanol

(The hydroxy group has higher priority than the amino group and is used to determine both the suffix and the numbering.)

PROBLEM 5.22

Name these compounds:

PROBLEM 5.23

Draw structures for these compounds:

- a) Diethylammonium bromide
- b) N-Methyl-3-(1-methylpropyl)-2-octanamine

Amines are polar compounds because of the presence of the nitrogen. Their melting and boiling points are higher than those of hydrocarbons of similar molecular mass. Like alcohols, primary and secondary amines are capable of forming hydrogen bonds, although the strength of the hydrogen bond is somewhat weaker in the case of an amine because nitrogen is less electronegative than oxygen. As a result, the boiling points of primary and secondary amines are somewhat lower than those of a similar alcohol. For example, butylamine boils at 78°C, and 1-butanol boils at 117°C. Because they have no hydrogens bonded to the nitrogen, the molecules of a tertiary amine do not form hydrogen bonds to each other, so the physical properties of tertiary amines resemble those of ethers. Amines of low molecular mass often have ammonia-like or fishy odors, and

some have quite unpleasant odors. Perhaps you can imagine the odors of cadaverine and putrescine:

Amines occur widely in nature, both in plants and animals. Natural amines, such as epinephrine (adrenaline), are often physiologically active in animals, as are some synthetic amines, such as amphetamine. Those that occur in plants, such as nicotine and morphine, are called **alkaloids** because they are basic and can be isolated by extraction with acid. When plant matter is extracted with aqueous acid, the amines are protonated according to the following equation:

$$RNH_2 + HC1 \implies RNH_3 \stackrel{+}{Cl}$$

The resulting salts dissolve in the aqueous solution and can easily be separated from the rest of the plant material.

Review of Mastery Goals

After completing this chapter, you should be able to:

- Provide the systematic (IUPAC) name for an alkane. (Problems 5.24 and 5.26)
- Draw the structure of an alkane whose name is provided. (Problem 5.25)
- Name a complex group. (Problem 5.30)
- Name a cycloalkane, an alkene, an alkyne, an alkyl halide, an alcohol, an ether, or an amine. (Problems 5.24, 5.29, 5.30, 5.33, 5.34, and 5.43)

Click Mastery Goal Quiz to test how well you have met these goals.

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- Draw the structure of a compound containing one of these functional groups when the name is provided. (Problems 5.25, 5.31, and 5.35)
- Predict the approximate physical properties of a compound containing one of the functional groups discussed. (Problems 5.36, 5.37, 5.38, 5.39, 5.44, 5.45, and 5.46)

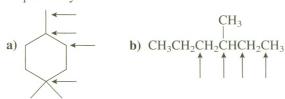
Additional Problems

5.24 Name these compounds:

$$\begin{array}{c} CH_2CH_3\\ |\\ \textbf{b}) \ CH_3CH = CHCHCH_2CH_3 \end{array}$$

- **5.25** Draw structures for these compounds:
 - a) 5-Ethyl-4-methylnonane
 - b) 2-Methyl-1,3-hexadiene
 - c) 3-Methylcyclopentanol
 - d) 3-Octyne
 - e) sec-Butylcyclohexane
 - f) tert-Butyl alcohol
- **5.26** Name the five isomers of C_6H_{14} .

5.27 Indicate whether each of the indicated carbons is primary, secondary, tertiary, or quaternary:



- **5.28** Draw compounds that meet these requirements:
 - a) A primary alcohol
- b) A tertiary alcohol
- c) A secondary alkyl chloride
- d) A secondary amine
- **5.29** What is wrong with the names given for these compounds? Provide the correct name for each.

2-Ethyl-2-pentene

3,4,9-Trimethyldecane

3-Cyclohexylpropane

1,3,4-Trimethylcyclopentane

1-Chloro-2-cyclopentene

1-Pentyn-4-ol

2-2-Methylbutylcyclopentanol

1-Methyl-1-pentenamine

1-Methylpentanol

5.30 Name these compounds:

- 5.31 Draw structures for these compounds:
 - a) 1,5-Dibromo-2,2-dichloro-4-ethyl-4-methyl-3-hexanol
 - b) 2,2,5,5-Tetramethylcyclohex-3-enol
 - d) 1,2-Cyclopentanediol
 - f) N,N-Diethylbutylamine
 - h) 5-(1,2,2-Trimethylpropyl)nonane
- c) tert-Butylamine
- e) Dibutyl ether
- g) 3-Isobutylcyclopentanol

5.32 Menthol is a component of oil of peppermint. Label each carbon of menthol as primary, secondary, tertiary, or quaternary. Should menthol be classified as a primary, secondary, or tertiary alcohol?



Menthol

5.33 Provide systematic names for these naturally occurring compounds:

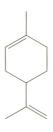


$$\begin{array}{c|cccc} OH & OH & OH \\ \hline b) & | & | & | & \\ CH_2-CH-CH_2 & & & \\ \end{array}$$
 Glycerol (obtained from fat)

- f) H₂NCH₂CH₂CH₂CH₂CH₂NH₂ Cadavering
- g) $CH_3(CH_2)_2CH$ =CHCH= $CH(CH_2)_8CH_2OH$ (so

Bombykol (sex attractant of the female silkworm moth) BioLink (§

5.34 The systematic name for the —CH=CH₂ group is ethenyl. Provide a systematic name for limonene, which is found in lemons and other citrus fruits.



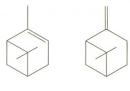
Limonene

BioLink (

- **5.35** Vitamin A alcohol is 3,7-dimethyl-9-(2,6,6-trimethyl-1-cyclohexenyl)-2,4,6,8-nonatetraen-1-ol. Draw the structure of vitamin A alcohol.
- **5.36** Explain which compound has the higher melting point:
 - a) Cyclopentane or pentane
 - b) 1-Pentanol or pentane
- **5.37** Explain which compound has the higher boiling point:
 - a) Octane or nonane
- b) Nonane or 3-nonene
- c) 1-Nonyne or 1-nonanol
- d) Trimethylamine or propylamine
- e) Cyclopentanol or diethyl ether
- f) 1-Butene or 1-butyne
- g) 1-Chlorobutane or 1-pentanol
- h) Cyclopentylamine or cyclopentanol
- **5.38** Chloroform, CHCl₃, is a common solvent in the organic laboratory. It is not miscible with water, so a mixture of these two solvents forms two layers. Which solvent do you expect to form the lower layer?
- **5.39** Predict which of these compounds has the higher solubility in water:
 - a) 1-Butanol or 1-chlorobutane
- **b)** 1-Butanol or 1-hexanol
- c) Pentane or diethylamine
- **5.40** While working in the chemical stockroom, you discover an unlabeled bottle containing a liquid compound. You carefully smell the liquid and discover that it has a fishy odor. What functional group do you suspect the unknown compound contains? What simple chemical test could you do to confirm the presence of the suspected functional group?



5.41 Turpentine, obtained from pine trees, is composed primarily of α -pinene and β -pinene. Explain whether you expect turpentine to mix with water. If a paint dissolves in turpentine, what does this suggest about the structure of the paint?



 α -Pinene

 β -Pinene

5.42 The structure of a typical fat is shown here. Estimate the energy content of fat compared to the other compounds discussed in the Focus On box on p. 146 and explain your reasoning.



$$\begin{array}{c} O \\ \parallel \\ CH_2 - OC(CH_2)_{16}CH_3 \\ \mid \quad \quad \cup \\ CH - OC(CH_2)_{14}CH_3 \\ \mid \quad \quad \cup \\ CH_2 - OC(CH_2)_7CH = CH(CH_2)_7CH_3 \end{array}$$

Problems Using Online Three-Dimensional Molecular Models

- **5.43** Name these compounds.
- **5.44** Explain which compound has the higher boiling point.
- Explain which compound has the higher melting point.
- **5.46** Explain which compound has the higher solubility in water.

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